Adsorbed Soda Investigations at Alunorte

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Abstract

In an effort to better close the soda balance at Alunorte, it was noted that the losses via adsorption were not being recorded. To improve upon this, laboratory tests were conducted to determine the adsorption slope of Alunorte residue to enable quantification of this loss. A new experimental method, designed to enable adsorption slope determination somewhat easier than the conventional methodology is reported. Further to this methodology, it is shown that carbonate is leaching from the residue, and hypotheses are put forward to explain this phenomenon. Utilization of the predicted adsorption slope indicates the soda loss to be of the order of 2 kg NaOH/t, yet considerations are also presented regarding the need to consider kinetic impacts of adsorption, given the reduced residence time of residue washing achieved by press filter technology.

Keywords: bauxite residue, soda adsorption, soda loss minimization.

1. Introduction

Ideally, all the soda is recycled in the Bayer circuit; the losses through output streams must be minimized to achieve better cost curve positioning and reduced environmental footprint. A comprehensive evaluation of the main forms of soda loss is fundamental for process performance evaluation and improvement opportunity identification. Recent process management initiatives at Hydro Alunorte to elucidate unaccounted soda losses have led to the recognition that soda adsorbed on bauxite residue was lacking monitoring and control.

Soda adsorption parameters for bauxite residue were first obtained experimentally by Michael Thornber and David Binet [1]. They introduced the assumption of zero soda adsorption in residue in contact with liquor solutions at alkali concentration (TA) of 2 $g.L^{-1}$ and initially proposed an adapted Langmuir equation to describe the relationship between adsorption and liquor TA. This equation provided an overestimated number of adsorption sites for the actual surface area available indicating that DSP adsorbs/desorbs Na^+ both from the surface and from within the cages of its mineral structure [1] (see Figure 1 below [2]).

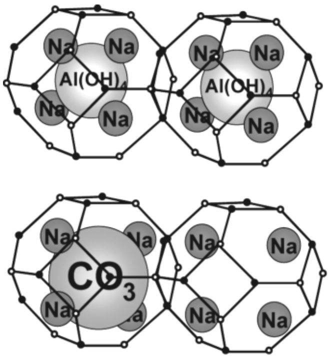


Figure 1. Model of DSP structure highlighting pores where sodium hydroxide may be able to adsorb/desorb [2].

The adsorption data obtained was thus applied to an empirical equation (Equation 1) and the slope S determined by linear regression [1].

$$Adsorption\ Na_2O = S\ (log_{10}\, c_{TA} - log_{10}\, 2) \qquad (1)$$

where:

Adsorption Na_2O is the g of Na_2O adsorbed per 100 g of residue
c_{TA} is the equilibrium concentration of total alkali, in g.L^{-1} Na_2CO_3

The level of soda adsorption affinity and saturation are thought to depend on mineral type, morphology and particulate surface area, as well as internal area in the case of minerals with zeolite structure like sodalite or cancrinite [1] [2]. Bauxite residue at Hydro Alunorte is composed mostly of the hematite and goethite, desilication product (DSP), and some anatase. Typical elemental composition is provided in Table 1. Process conditions of bauxite residue washing units also affect the degree of soda adsorption and desorption.

Table 1. Bauxite residue elemental composition at Hydro Alunorte (values in % m/m).

Fe_2O_3	Al_2O_3	SiO_2	Na_2O	LOI*	TiO_2	Others
32.6	23.1	17.1	9.8	9.1	5.6	0.3

*LOI stands for loss on ignition, the total mass of compounds volatilized at up to 1000°C.

Teemu Kinnarinen et al. [3] have reported differences on soda recovery from bauxite residue when submitted to press filtration at different temperatures and pressures, which was attributed to desorption and dissolution of Na^+. At Hydro Alunorte, drum and press filtration units operate with different washing residence times and solids concentrations (65 and 78 % solids, respectively).

Using plant-sourced or synthetic bauxite residue, the experiments of Thornber and Binet [1] consisted of a progressive desorption routine with multiple steps, involving: residue dilution into water, agitation for 30 minutes, centrifugation and removal of the supernatant liquor solution. All of the work was performed using 70 mL samples, constant temperature of 55 °C (including centrifuging), and an in-house liquor specific gravity correlation to assist with the mass balancing.

The samples were assumed to reach adsorption equilibrium at each dilution step, but no tests were presented to sustain this assumption. The study does not mention whether any differences existed between the experiments with different solids concentrations, suggesting that no difference was noted. Further, due to the significant amount of soluble soda removed in the early stages of washing, determining the adsorbed soda at the higher concentrations was particularly erroneous.

In a similar study, Keddon A. Powell et al. [4], identified adsorption parameters of mineral components of bauxite residue, but with another experimental procedure and using a linearization of the Langmuir equation to correlate experimental results. As with Michael Thornber and David Binet [1], Powell et al. [4] also attributed the higher than expected adsorption capacity of DSP (18.2 Na^+ atoms per nm²) to internal exchange sites [4]. The experiments approached adsorption "from below", with 3 g residue samples and 9 mL of diluted spent liquor. The studies here were conducted at room temperature, with 3.5 hours of residence time to establish equilibration, but again, no data was provided suggesting this was sufficient. The authors do not indicate the level of statistical rigor employed in their work, nor specify the SG equation used to convert concentration values into mass basis.

Regarding what actually is adsorbing to the residue, Thornber and Binet [1] provide plots for TA, TC and Alumina adsorption which suggest that the alumina does not adsorb. Nonetheless, the authors chose to correlate the soda adsorption against the TA, without consideration for what exactly is driving the adsorption, perhaps yielding to the general idea that the TA is a general marker for how concentrated the solution is. Powell et al [4] noted that the analyte which experienced the greatest drop via the adsorption test was NaOH, but did not comment further regarding the other analytes or specific quantitative differences.

The focus of this study is to identify the equilibrium adsorption slope for Alunorte residue at room temperature, using techniques from both of the key works in the open literature and reported here. As part of this work, the time for equilibration at ambient conditions and the adsorption impact on liquor causticity is also evaluated. The adsorption function in terms of TA and/or TC was pursued to enable a better routine monitoring of soda losses. Subsequent to this investigation and given the shift in residue disposal technologies whereby the solids content increased dramatically, the study also aimed to investigate if any differences in adsorption could be observed for different solids concentration environments.

2. Research Methodology

2.1. Bauxite residue preparation

Firstly, the bauxite residue was collected from last washer underflows on site and washed to remove all initial adsorbed soda through a procedure based on Thornber and Binet [1], detailed in Figure . The residue was washed with a solution of TA 2 $g.L^{-1}$ (prepared using analytical grade Na_2CO_3) instead of pure water to preserve the crystal structure of DSP [1]. Exceptionally the residue from tests to determine adsorption equilibration time was washed with a solution of higher causticity. The equilibrium concentration of species CO_3^{-2} and HCO_3^- in the first wash solution was ignored and is perhaps a weakness of this study.

Bauxite residue and wash solution were mixed in a proportion of 1:1 (m/m); the slurry was stirred for 3 hours and then filtered. The electrical conductivity (EC) of the filtrate, which is linearly proportional to its alkalinity at low concentrations, was measured in triplicate and compared to the value found for the wash solution – while the EC of the former is much higher than the latter, the residue must be washed again with a new batch of TA 2 $g.L^{-1}$ solution. The wash loop would conclude when residue EC stabilized and equalized to wash solution EC. This criterion confirms what is assumed to be complete soda desorption and, after that, the residue is completely filtered.

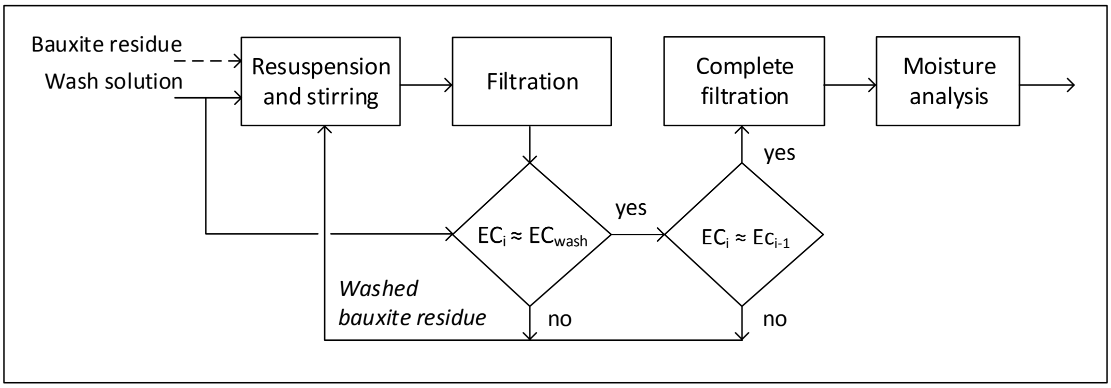


Figure 2. Bauxite residue wash procedure.

The possibility of crystallographic/surface area changes caused by high-temperature drying of bauxite residue was not clear. To combat against any possible differences incurred by drying residue, tests were performed using solids maintained at room temperature, with residual moisture. Still, moisture could reduce to some extent between the wash and the time of the tests. Therefore, after filtration and before sample preparation, the slurry was measured for moisture content by a halogen moisture analyzer, to inform the dry mass of solids added and to obtain the residual soda content from the wash solution.

2.2. Soda Adsorption Test Methodology

For each sequence of tests, spent liquor was collected on site from test tanks. Both high and low causticity liquors (with TC/TA from 80 to 95 %, and 60 %, respectively) were prepared by dilution of plant liquor with deionized water, and analytical grade Na_2CO_3 solutions. The TA values of the liquors prepared were set between 10 and 100 $g.L^{-1}$. A room-temperature adsorption test procedure (Figure 3) based on Powell et al. [4] was performed to:

a. estimate the time required to reach soda adsorption equilibrium, using samples with known solids content and known start liquor TA and TC;
b. obtain soda adsorption values for a fixed test duration with samples of known solids content, liquor TA and TC.

For step (a), measured masses of wet, washed bauxite residue (with known moisture content) and of high-causticity liquor of TA 20 $g.L^{-1}$ were combined targeting 50 % solids into 250 mL Nalgene bottles. The samples, made in duplicate, were placed in a bottle-rolling apparatus for different times (1, 2, 4, 8 and 20 hours) and then filtered.

The resulting filtrates were subsampled in triplicate and titrated to obtain TC and TA. The start liquor of TA 20 $g.L^{-1}$ served as a control for titration results; its subsamples were interspersed between finish samples on the titration line to guarantee the reliability of the titration results. In transforming the concentration data to a mass basis (i.e. $g.L^{-1}$ to $g.g^{-1}$) to calculate the adsorption, the Mulloy-Donaldson SG correlation was utilized [6]. Some direct comparison was made with crudely measured liquor SG and found to be approximately equivalent.

Step (b) occurred similarly: known masses of liquor (with certain TAs and causticities) and wet residue (with known moisture) were combined into 250 mL Nalgene bottles in duplicates, with samples of 40 % and 60 % solids at each batch test, to check the impact of solids concentration on adsorption rate. After stirring for 4 hours (sufficient residence time to achieve equilibrium) the samples were filtered, subsampled and titrated sequentially; each replicate alternating with its corresponding starting liquor analyte, that served as a control to account for the analytical accuracy.

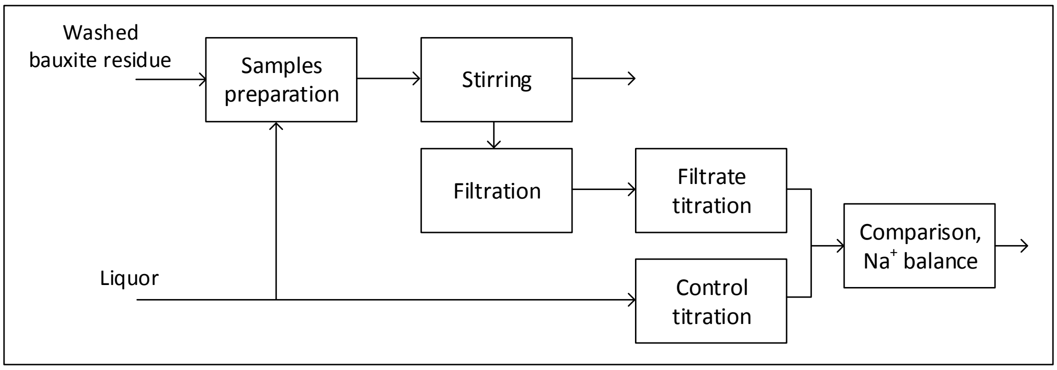


Figure 3. Adsorption test procedure.

The true starting TC and TA of each test sample were corrected to accommodate the effect of bauxite residue moisture. For a given sample, the corrected initial TC c_{iTC} (in g.L^{-1}) accounts for the initial mass of total caustic in residue moisture m_{moTC} (in g) and in liquor $m_{liquorTC}$ (in g):

$$c_{i_{TC}} = \frac{m_{i_{TC}}}{V_i} = \frac{m_{mo_{TC}}+m_{liquor_{TC}}}{V_i} \tag{2}$$

The total initial volume V_i and the caustic masses were obtained from volumetric concentrations ($c_{liquorTC}$ and c_{moTC} in g.L^{-1}), liquor weight m_{liquor}, wet mass of bauxite residue m_{res}, in g, residue moisture mass fraction x_{mo}, and specific gravities in g.mL^{-1} based on the Mulloy-Donaldson correlation [6] (SG_{liquor}, SG_{mo} and SG_i).

$$m_{liquor_{TC}} = c_{liquor_{TC}} \cdot \frac{m_{liquor}}{SG_{liquor}} \tag{3}$$

$$m_{mo_{TC}} = c_{mo_{TC}} \cdot \frac{m_{res} \cdot x_{mo}}{SG_{mo}} \tag{4}$$

$$V_i = \frac{m_{liquor}+m_{res} \cdot x_{mo}}{SG_i} \tag{5}$$

The adsorbed soda values m_{adsTC} for each sample were calculated according to:

$$m_{ads_{TC}} = c_{i_{TC}} \cdot \frac{m_i}{SG_i} - c_{f_{TC}} \cdot \left(\frac{m_i - m_{ads_{TC}}}{SG_f}\right) \tag{6}$$

where m_i is the initial total mass of sample, and the subscript f indicates the final solution, i.e. after the adsorption test. Rearranging:

$$m_{ads_{TC}} = \left(c_{i_{TC}} \cdot \frac{m_i}{SG_i} - c_{f_{TC}} \cdot \frac{m_i}{SG_f}\right) . \left(1 - \frac{c_{f_{TC}}}{SG_f}\right)^{-1} \tag{7}$$

The final processing was on a Na_2O basis, but was calculated using the TC of the liquors. Soluble silica was also measured, via the molybdate blue titration method, in some samples after the tests to check against DSP dissolution.

2.3. Weighted Least Squares (WLS)

The regression of adsorbed soda versus equilibrium liquor TC with logarithmic fit was done through WLS, to account for differences of analytical resolution depending on the range of liquor concentration of each sample: in the experiments conducted; the lower the concentration, the higher the measurement errors and uncertainties.

Based on Equation 1 [1], the soda adsorption in bauxite residue ads was described as linearly proportional to the logarithm of liquor TC c_{TC}, at equilibrium conditions, with a constant slope S:

$$ads = S \cdot \log_{10}\left(\frac{c_{TC}}{2}\right) \tag{8}$$

Expressing in matrix form, the predicted adsorption values $\hat{Y}$ are:

$$\hat{Y} = X \cdot \hat{\beta} \tag{9}$$

For n measurements, $\hat{Y}$ is a $n \times 1$ matrix, $\hat{\beta}$ is a 1×1 matrix for the estimated slope, and:

$$X = \begin{bmatrix} x_0 \\ \vdots \\ x_n \end{bmatrix}_{nx1} = \begin{bmatrix} log_{10}\left(\frac{c_{TC_0}}{2}\right) \\ \vdots \\ log_{10}\left(\frac{c_{TC_n}}{2}\right) \end{bmatrix}_{nx1} \tag{10}$$

Using basic statistical methods [7], the best estimated slope is obtained by WLS when the difference between $\hat{Y}$ and the actual adsorption values Y are minimized. In matrix form:

$$X^T \cdot W \cdot (Y - \hat{Y}) = 0 \tag{11}$$

For heteroskedastic data, W is a $n \times n$ weights matrix as:

$$W = \begin{bmatrix} w_0 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & w_n \end{bmatrix} \tag{12}$$

And the slope obtained by WLS ($\hat{\beta}_{WLS}$) is equal to:

$$\hat{\beta}_{WLS} = (X^T \cdot W \cdot X)^{-1} \cdot X^T \cdot W \cdot Y \tag{13}$$

The WLS weights w_x were defined as the inverse of $s_{\bar{x}}$, which are the errors propagated to the masses of adsorbed soda using standard propagation of error techniques [8]:

$$\mathrm{w_x} = \frac{1}{s_{\bar{x}}{}^2} \tag{14}$$

For each sample prepared, the error of the measured masses was considered 0.01 g in line with the measurement error of the equipment utilized. Standard errors of liquor TA and TC averages, from titrations, were calculated from standard deviations of the triplicate results. The errors of SG correlations and residue moisture TC were not taken into consideration, thus the errors shown represent a lower limit to the real ones. The actual implementation of these calculations was done using the Real Statistics Resource Pack software (Release 5.6) [9] add-in for Excel®.

2.4. Titration Comments

The TA and TC concentrations liquor solutions before (t = 0) and after adsorption tests were measured through Metrohm® automated titrators using modified Watts-Utley method [5] (with no KF addition nor alumina quantification).

Liquors and filtrates of the adsorption tests were sometimes near the detection limits of the original Metrohm® Tiamo™ algorithms employed on routine liquor titrations. Therefore, a significant portion of titration raw data was processed via customized algorithms:

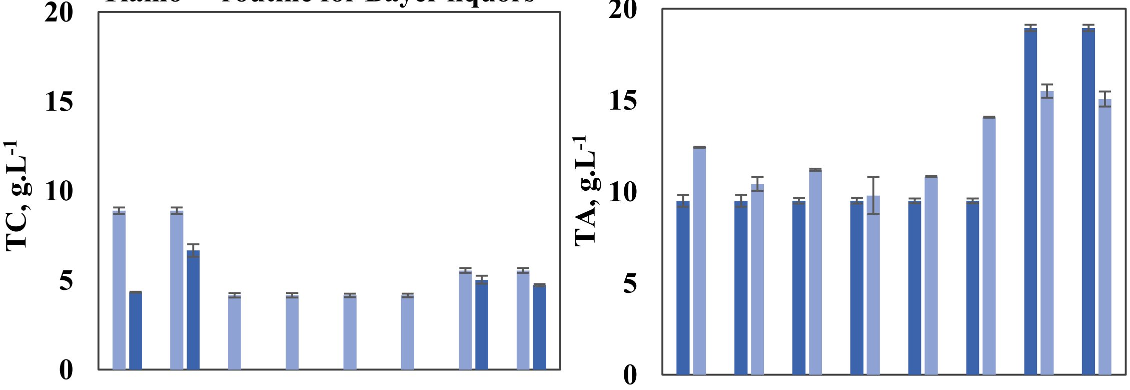
- First titration endpoints (for TC determination) were estimated with Gran methodology, where the lower limit on pH was set at 10.3 and the maximum was optimized for each sample (by minimizing the x-intercept error of the Gran plot [10] endpoint volumes). The results were compared with a method of 1st derivative minimization using numerical centered differences on the raw pH versus volume data and different polynomial fitting schemes on the numerical derivative data.
- Second titration endpoints (relative to carbonate) were estimated by 2nd derivative root estimation using numerical centered differences on both the raw pH versus volume data and the 1st derivative data, with different polynomial fitting schemes.

3. Results and Discussion

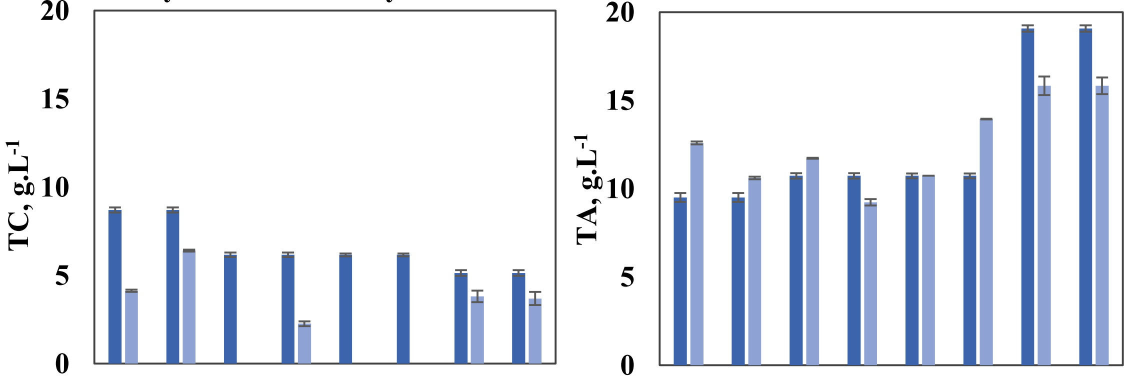
3.1. Titration Data Re-processing and Carbonate Leaching

Figure *4* presents TC and TA results before and after adsorption tests run with samples at the lowest start liquor concentrations, obtained from the aforementioned methods of processing automatic titration data. The Gran methodology allowed the detection of TC values as low as 1.3 g.L^{-1} with standard errors up to 0.3 g.L^{-1} for two different triplicates of liquor analysis, while the conventional algorithms could not detect the end point. This is believed to be associated with the fact that the Gran method uses more data further from the endpoint in endpoint determination, when compared to inflection methods.

Tiamo™ routine for Bayer liquors



TC by 1st Inf and TA by 2nd Inf



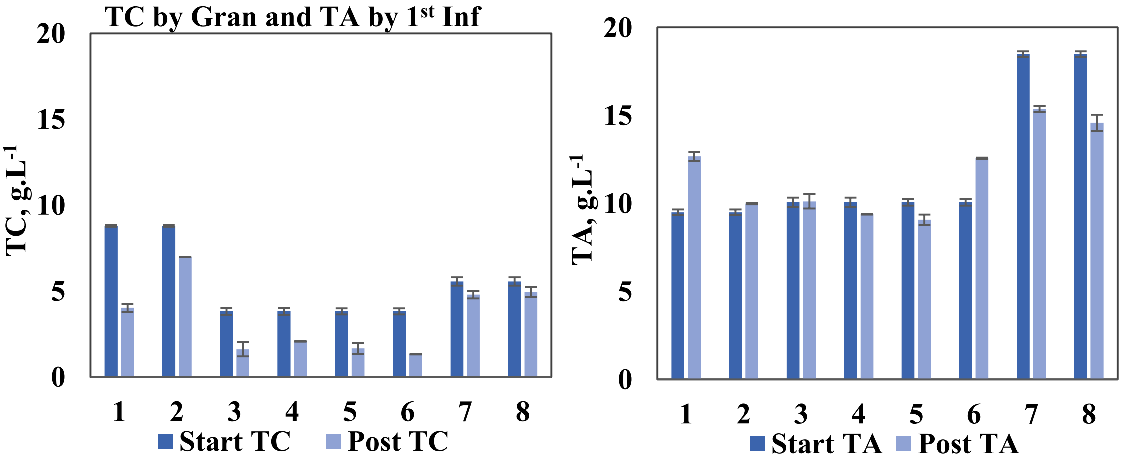


Figure 4. TC and TA of liquor samples obtained by Metrohm, Gran and Inflection methods.

Further, the application of customized titration data re-processing methods also helped to confirm the occurrence of carbonate leaching, given the unexpected observations of liquor TA increase or stagnation in liquor phases after adsorption tests, while the TC values reduced. The phenomenon was confirmed through different titration processing methods and was shown in samples with both high and low starting TC/TA ratios.

The initial justification considered for the increase in carbonate was DSP dissolution (note that the sample bottles were closed disallowing carbonation from air), but subsequent analyses of silica in sample solutions after the tests have indicated essentially negligible dissolution. In terms of carbonate specific leaching from the DSP without breaking down the zeolitic structure, this is considered very unlikely due to the size difference between the carbonate anion and the aluminosilicate pore openings. Earlier work by Smith et al. [2] has suggested it *may* be possible for carbonate to convert to CO_2 and escape, but this was for water washing, not low caustic adsorption work. Presently, the exact mechanism for this result is poorly understood.

The test work conducted was somewhat unique compared to the literature, in that the solid used has a large amount of carbonate DSP and the liquor used, being based off plant liquor, has a very low carbonate content. It was suspected, albeit by unknown mechanisms, that these two attributes could be contributing to the carbonate leach. Further, this result confirmed that, at least for Alunorte liquor and solids, the carbonate (and therefore the TA) should not be considered as adsorbing. This then led to the definition of adsorbed soda using TC only (remembering that free caustic of liquor samples was not available due to no alumina analysis with the titration methods).

3.2. Adsorption Equilibrium Tests

Four duplicate samples, prepared with 1:1 (m/m) wet bauxite residue (30 % moisture) and liquor solution of TA = 20 g.L^{-1}, were maintained with agitation for 1, 2, 4, and 20 hours. The corresponding soda adsorption results (Figure 5) overlap within the same confidence interval.

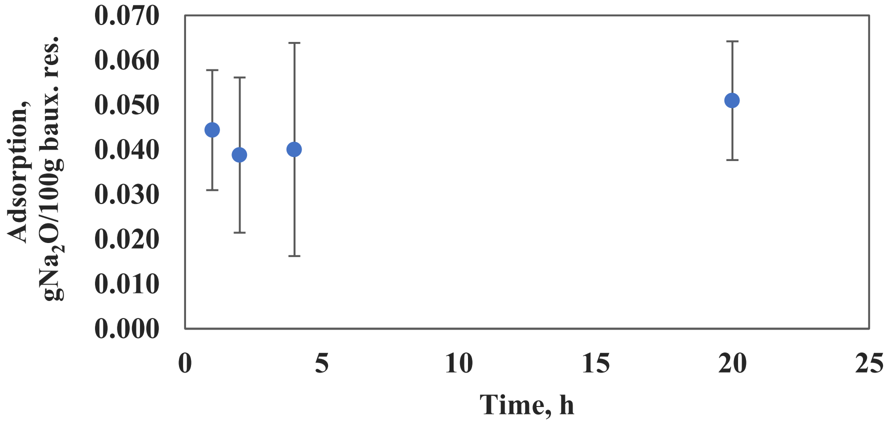


Figure 5. Adsorbed soda values at 1, 2, 4 and 20-hour tests.

According to these observations, the equilibrium has essentially been established earlier than the shortest test runs allowing 4 hours of residence time for the subsequent tests.

The results suggest that kinetics do not limit soda desorption extensively in moderate or high-residence time vessels such as decanters. However, they are not conclusive in determining the kinetic impacts of washing conditions in modern bauxite residue treatment technologies such as automated press filters. The evaluation of soda adsorption or desorption progress at shorter time intervals (under 60 minutes) with temperatures above ambient, could perhaps be carried out in a laboratory-scale filtration apparatus analogous to that described by Robert LaMacchia et al. [11].

3.3. Determination of Adsorption Equilibrium Slope

The WLS regression performed for sample points of 40 % solids, 60 % solids, and all values combined are presented (Figure 6). The linear regression was fixed through the origin, consistent with zero adsorption at TA 2 g.L^{-1}. The resultant coefficients and their standard errors are provided in Table 2.

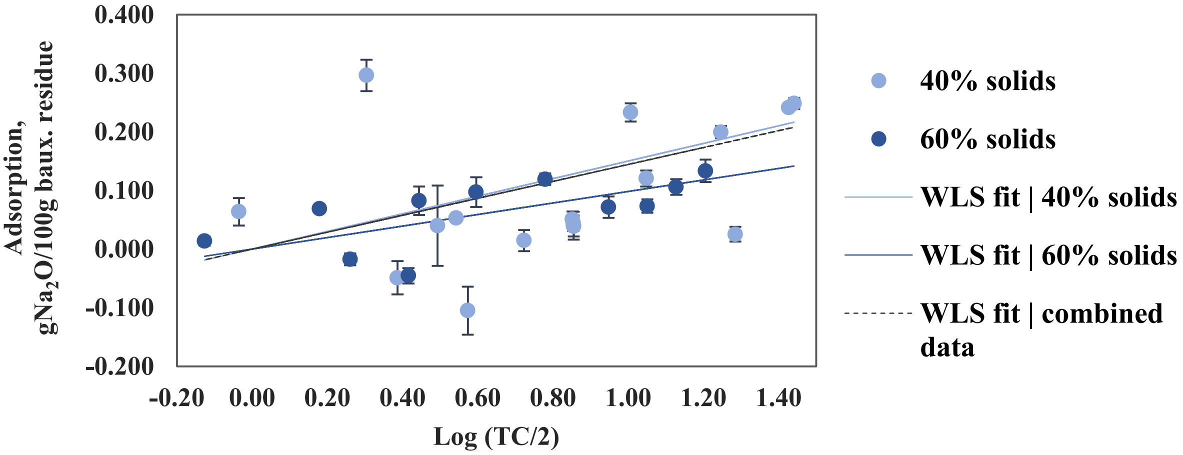


Figure 6. WLS regression for soda adsorption in bauxite residue vs. log(TC/2).

Table 2. Slope coefficients from WLS regressions of soda adsorption vs. log(TC/2).

Data set	Slope coefficient	Standard error
40 % solids samples	0.150	0.012

60 % solids samples	0.098	0.024
Combined data (40 % and 60 %)	0.144	0.010

Slope estimations with their respective standard errors for 60 % solids and 40 % solids concentrations, overlap at the 95 % level of confidence; so there is no indication in this data that the slopes are different for different solids loading.

The adsorption slope coefficient found for the complete data set was applied to the average plant data, so as to obtain an estimative for adsorbed soda loss. Given typical TCs at the output of bauxite residue, a residue/bauxite specific consumption of ~0.3 and overall alumina recovery of ~95 %, the slope would indicate ~2.0 kg of NaOH lost per tonne of alumina.

Comparing with results of other Fe-rich, Jamaican bauxite residues, the slope coefficient found for the overall experimental data is lower than values that correspond to high-hematite or high-goethite residues (0.314 ± 0.002 and 0.204 ± 0.003 g Na_2O/100 g, respectively) [10]. An intermediary slope value would be expected for this study, as the iron minerals present in the bauxite consumed at Alunorte are generally both hematite and goethite [11], which practically remain undissolved at low-temperature gibbsite digestion [12]. Further adsorption tests and residue characterization (in regard to mineralogy and particle size distribution) would be required to evaluate the contribution of DSP content to the adsorption slope and for more conclusive comparisons with the literature.

4. Conclusions

The soda adsorption on bauxite residue at Alunorte has been investigated through the development of an experimental method based on open literature techniques. The method has been applied to observe adsorption kinetics and adsorption equilibrium versus liquor composition. The results have shown that liquor TC/TA can decrease during the adsorption for high TC/TA start liquors, which perhaps corresponds to carbonate leaching from the DSP structure. Further, the test work has indicated that at 25 °C, the soda adsorption reaction has equilibrated after one-hour residence time. The reported slope, together with standard discharge liquor concentrations, suggests a soda loss on the order of 2 kg/t. It is essential that for this reporting, the TC (and not the TA) be used due to possible complications from carbonate leaching.

5. Acknowledgments

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